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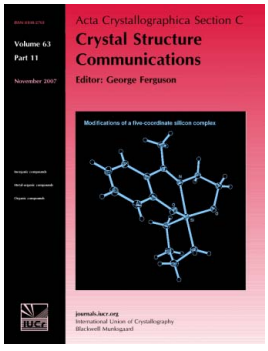

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Azetidine, pyrrolidine and hexamethyleneimine at 170 K

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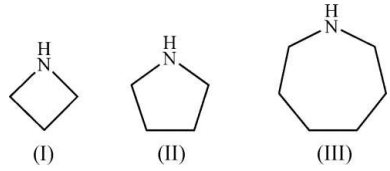
The crystal structures of the cyclic amines azetidine (C_3H_7N), pyrrolidine (C_4H_9N) and hexamethyleneimine (homopiperidine, $C_6H_{13}N$), of the series $(CH_2)_nNH$, with n = 3, 4 and 6, respectively, have been determined at 170 K, following *in situ* crystallization from the melt. These structures provide crystallographic data to complete the homologous series of cyclic amines $(CH_2)_nNH$, for n = 2–6. Azetidine and pyrrolidine contain chains propagating along 2_1 screw axes, in which the molecules are linked by co-operative N—H···N hydrogen bonds. Azetidine has two molecules in its asymmetric unit, while pyrrolidine has only one. Hexamethyleneimine contains tetrameric hydrogen-bonded rings formed about crystallographic inversion centres, with two molecules in its asymmetric unit. The observation of crystallographically distinct molecules in the hydrogen-bonded chains of azetidine and cyclic hydrogen-bonded motifs in hexamethyleneimine is consistent with expectations derived from comparison with monoalcohols forming chains or rings by co-operative O—H···O hydrogen bonds. The next member of the cyclic amine series, heptamethyleneimine, forms a cubic plastic phase on cooling from the melt.

Comment

Contemporary developments in instrumentation and techniques for *in situ* crystallization have greatly simplified the task of obtaining diffraction data for low-melting materials (Boese & Nussbaumer, 1994; Davies & Bond, 2001). This paper describes single-crystal X-ray structures for the cyclic amines azetidine, (I), pyrrolidine, (II), and hexamethyleneimine (homopiperidine), (III), all of which are liquid under ambient conditions. Together with the previously reported structures of aziridine (Mitzel *et al.*, 1997) and piperazine (Parkin *et al.*, 2004), these structures provide crystallographic data to complete the homologous series of cyclic amines $(CH_2)_nNH$, for n = 2–6.

In each structure of the series, molecules are linked by co-operative N—H···N hydrogen bonds with comparable geometric characteristics (Tables 1–3). Aziridine (n = 2), azetidine (n = 3; Fig. 1), pyrollidine (n = 4; Fig. 2) and piperazine (n = 5) all form one-dimensional hydrogen-bonded chains. In these last two structures, the chains propagate along



(I) (II) (III)

2_1 screw axes in the space group $P2_1/c$, with one molecule in the asymmetric unit (Fig. 3). In azetidine, the chains also propagate along 2_1 screw axes in $P2_1/c$, but with two crystallographically distinct molecules in each chain (Fig. 4). Thus, every second molecule along the chain is related by the 2_1 screw operation, and every fourth molecule is related by translation along b. Aziridine crystallizes in the space group $P\overline{1}$ with three crystallographically distinct molecules in each hydrogen-bonded chain. The chain conformation has approximate 3_1 screw symmetry (Fig. 5), with every third molecule related by translation along b. In hexamethyleneimine (Fig. 6), the molecules form tetrameric rings with a closed cycle of co-operative N—H···N hydrogen bonds. The rings are formed about crystallographic inversion centres in the space group $P2_1/n$, with two of the four molecules of the tetramer being crystallographically distinct (Fig. 7).

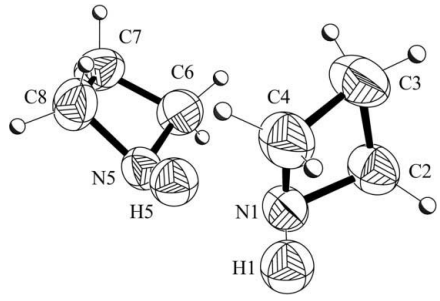


Figure 1
The two molecules in the asymmetric unit of azetidine, (I), with displacement ellipsoids drawn at the 50% probability level, except for H atoms bound to C atoms, which are shown as small spheres of arbitrary radii.

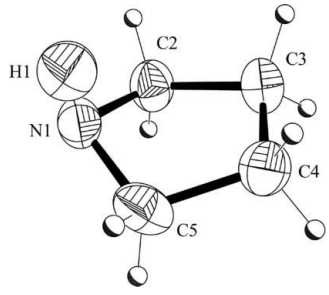


Figure 2
The molecular structure of pyrrolidine, (II), with displacement ellipsoids drawn at the 50% probability level, except for H atoms bound to C atoms, which are shown as small spheres of arbitrary radii.

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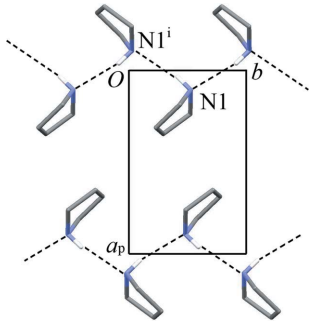

Figure 3
A view of pyrrolidine along the *c* axis, showing two chains linked by co-operative N—H···N hydrogen bonds (dashed lines) propagating along 2_1 screw axes parallel to the *b* axis. H atoms bound to C atoms have been omitted. [Symmetry code: (i) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$.]

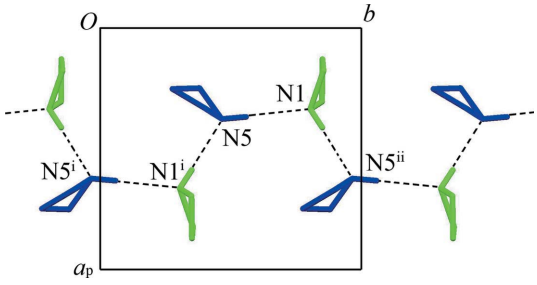

Figure 4
A view of azetidine along the *c* axis, showing one chain linked by co-operative N—H···N hydrogen bonds (dashed lines) propagating along a 2_1 screw axis parallel to the *b* axis. The two crystallographically distinct molecules and their symmetry equivalents are distinguished by their shading. H atoms bound to C atoms have been omitted. [Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$.]

The N—H···N hydrogen-bond motifs in the cyclic amines are reminiscent of those observed frequently in monoalcohols. For example, hydrogen-bonded chains exist in both the ambient-pressure (Jönsson, 1976) and high-pressure (Allan & Clark, 1999) polymorphs of ethanol, while the more bulky 3-ethyl-3-pentanol forms cyclic tetramers (Bond, 2006). The NH group resembles the OH group in that it can act simultaneously as a hydrogen-bond donor (albeit a worse one than OH; Steiner, 2002) and as an acceptor. Thus, extended chains and closed rings are expected motifs in both cases. For the monoalcohols, Brock & Duncan (1994) noted that the occurrence of structures with more than one crystallographically distinct molecule is anomalously high on account of frequent conflicts between the spatial requirements of O—H···O hydrogen bonds and the overall contraints of molecular close packing, *i.e.* that molecules are most often arranged about inversion centres, 2_1 screw axes or glide planes. Formation of extended O—H···O hydrogen-bonded chains in the monoalcohols requires that the O atoms are brought within *ca* 2.7–2.9 Å of each other. In the cyclic amines, the corresponding N···N distance is slightly longer (*ca* 3.1–3.2 Å). Within these contraints, O—H···O or N—H···N hydrogen-bonded chains might be compatible with molecular packing about 2_1 screw axes or glide planes, for example, as in pyrrolidine and

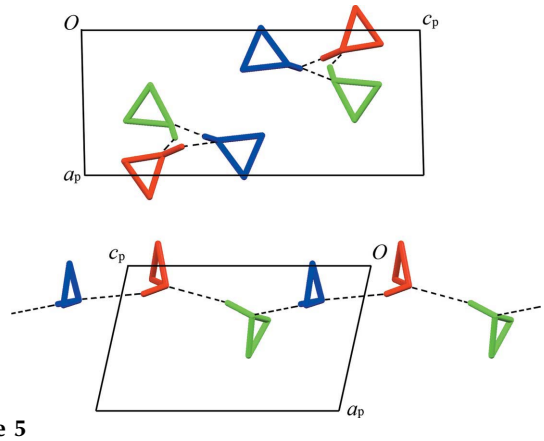

Figure 5
Perpendicular views of the hydrogen-bonded chains in aziridine (Mitzel *et al.*, 1997), showing the approximate 3_1 screw symmetry. The three crystallographically distinct molecules and their symmetry equivalents are distinguished by their shading. H atoms bound to C atoms have been omitted.

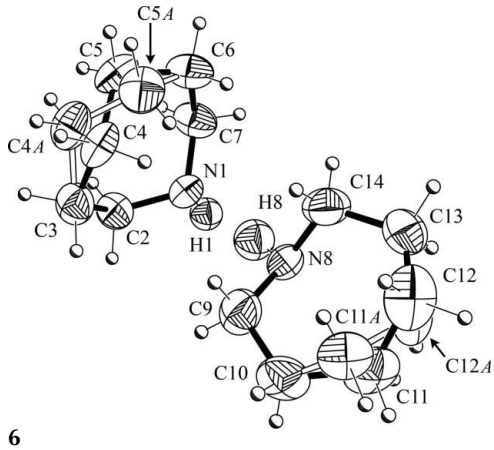

Figure 6
The two molecules in the asymmetric unit of hexamethyleneimine, (III), with displacement ellipsoids drawn at the 50% probability level, except for H atoms bound to C atoms, which are shown as small spheres of arbitrary radii.

piperazine. In other cases, however, such compatibility may not be assured, and the chain motifs are therefore much more likely [compared with structures in the Cambridge Structural Database (Allen, 2002) as a whole] to be formed either with more than one crystallographically disinct molecule, as in azetidine, or around screw or roto-inversion axes of order 3, 4 or 6, as approximated by aziridine. For more bulky molecules, cyclic motifs offer a further alternative. These are commonly tetrameric and may be formed in tetragonal space groups (*e.g.* 2-phenyladamantan-2-ol; Singelenberg & van Eijck, 1987) or about inversion centres with two crystallographically distinct molecules, as in hexamethyleneimine and 3-ethyl-3-pentanol (Bond, 2006). It has been observed that the packing arrangements of bulky alcohols can be made to resemble those of smaller alcohols on application of increased pressure. For example, the crystal structures of 2-chlorophenol and 4-fluorophenol at ambient pressure contain hydrogen-bonded chains propagating along 3_2 and $\overline{3}$ axes, respectively, while at high pressure both contain chains along 2_1 axes (Oswald *et al.*, 2005).

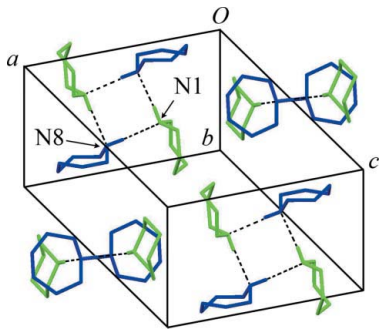

Figure 7
The unit-cell contents of hexamethyleneimine, showing tetramers linked by co-operative N—H···N hydrogen bonds (dashed lines). The two crystallographically distinct molecules and their symmetry equivalents are distinguished by their shading. H atoms bound to C atoms have been omitted.

The crystal structure of azetidine was used as a target in the third blind test of crystal structure prediction (CSP2004) organized by the Cambridge Crystallographic Data Centre (Day *et al.*, 2005). The two crystallographically distinct molecules provided difficulty in this exercise, and the correct structure was not present amongst the first three predictions of any of the participants. It was noted that the structure at 170 K appears to be a saddle point on the potential energy surface, with a low barrier for transformation to a postulated lower-symmetry structure in the space group $P\overline{1}$ with four molecules in the asymmetric unit.

Experimental

Single crystals of pyrrolidine and hexamethyleneimine were grown in 0.3 mm diameter glass capillaries at a temperature just below the melting point of the sample, using the manual zone-refinement technique described by Davies & Bond (2001). The diffraction patterns were indexed at a temperature just below the melting point from a series of images collected by rotation about the capillary axis, with the capillary remaining in the horizontal position in which the crystal was grown. Moving the capillary away from horizontal at this delicate stage resulted in loss of the crystal, while subsequent cooling (to 170 K) for data collection caused growth of multiple crystals. The orientation matrix established for the initial single crystal was retained and used throughout the data collection and integration, and any possible overlap with diffraction patterns from other crystal components was ignored. For both compounds, this strategy provided acceptable $R_{\rm int}$ values, although the relatively high R values for the refinement of hexamethyleneimine are likely to be attributable largely to more significant overlap in its diffraction pattern. Since there were clearly contributions from many crystals, however, the approximations associated with ignoring overlap completely were preferred to the approximations associated with integration on the basis of numerous partially overlapping components. It was not possible to grow suitable crystals of azetidine using the manual technique and crystallization was therefore achieved from a sample mounted in a 0.66 mm diameter capillary held at 170 K, using the laser-assisted zone-refinement technique of Boese & Nussbaumer (1994). Again, the diffraction pattern contained contributions from more than one crystal, but a single crystal could be indexed using the program *GEMINI* (Bruker, 2003) and integration on the basis of this single component provided good results. In all cases, the exact size of the crystal used for data collection is uncertain, and it is probable that the length along the capillary axis exceeds the size of the X-ray beam. This seems to have little influence on the final refined parameters (Görbitz, 1999). Following data collection at 170 K, further cooling of the crystals caused deterioration of the peak shapes for all three compounds, to the extent that no further useful data could be obtained. Attempts were made to crystallize the next member of the series, heptamethyleneimine, but this forms a plastic phase on cooling from the melt. The diffraction pattern could be indexed on the basis of a cubic lattice with dimension 11.647 (3) Å, but it was not possible to establish any definite structural model.

Compound (I)

Crystal data

C_3H_7N
M_r = 57.10
Monoclinic, $P2_1/c$
a = 9.507 (3) Å
b = 9.122 (3) Å
c = 9.790 (3) Å
β = 117.469 (4)°
V = 753.3 (4) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.06 mm^{-1}
T = 170 (2) K
1.00 × 0.33 (radius) mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
$T_{\rm min}$ = 0.688, $T_{\rm max}$ = 0.960
4439 measured reflections
1782 independent reflections
1144 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.035

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.162
S = 1.04
1782 reflections
83 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max}$ = 0.18 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.17 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N5—H5···N1	0.86 (2)	2.27 (2)	3.120 (2)	171.5 (15)
N1—H1···N5^{i}	0.87 (2)	2.24 (2)	3.102 (2)	174.4 (16)

Symmetry code: (i) $1-x, y+\frac{1}{2}, \frac{1}{2}-z$.

Compound (II)

Crystal data

C_4H_9N
M_r = 71.12
Monoclinic, $P2_1/c$
a = 8.6753 (8) Å
b = 5.2078 (5) Å
c = 10.7108 (10) Å
β = 110.451 (3)°
V = 453.41 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.06 mm^{-1}
T = 170 (2) K
0.35 × 0.15 (radius) mm

Data collection

Bruker–Nonius X8 APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
$T_{\rm min}$ = 0.853, $T_{\rm max}$ = 0.977
5429 measured reflections
900 independent reflections
760 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.026

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···N1^{i}	0.84 (2)	2.35 (2)	3.1716 (13)	163.7 (15)

Symmetry code: (i) $-x, y-\frac{1}{2}, \frac{1}{2}-z$.

Table 3
Hydrogen-bond geometry (Å, °) for (III).

D—H···A	D—H	H···A	D···A	D—H···A
N8—H8···N1	0.90 (3)	2.27 (3)	3.167 (3)	176 (3)
N1—H1···N8^{i}	0.90 (2)	2.25 (3)	3.150 (3)	175 (2)

Symmetry code: (i) $1-x, 1-y, -z$.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.110$
$S = 1.06$
900 reflections
50 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.16$ e Å^{-3}
$\Delta\rho_{min} = -0.13$ e Å^{-3}

Compound (III)

Crystal data

$C_6H_{13}N$
$M_r = 99.17$
Monoclinic, $P2_1/n$
$a = 11.0201$ (14) Å
$b = 10.3027$ (13) Å
$c = 12.7322$ (15) Å
$\beta = 114.110$ (5)°
$V = 1319.5$ (3) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.06$ mm^{-1}
$T = 170$ (2) K
0.35 × 0.15 (radius) mm

Data collection

Bruker–Nonius X8 APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
$T_{min} = 0.688$, $T_{max} = 0.981$
16092 measured reflections
2509 independent reflections
1824 reflections with $I > 2\sigma(I)$
$R_{int} = 0.051$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.083$
$wR(F^2) = 0.269$
$S = 1.12$
2509 reflections
173 parameters
14 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}

H atoms bound to C atoms were positioned geometrically and allowed to ride during refinement, with C—H = 0.99 Å and U_{iso}(H) = $1.2U_{eq}$(C). H atoms of the NH groups were located in difference Fourier maps and refined with isotropic displacement parameters. For azetidine and pyrrolidine, no restraints were required. For hexamethyleneimine, the two N—H distances were restrained to a common refined value with standard uncertainty 0.01 Å. Atoms C4, C5, C11 and C12 in hexamethyleneimine were modelled as disordered, each as two components with a site-occupancy factor of 0.5. The C—C bonds in this region (12 in total) were restrained to a common refined value with standard uncertainty 0.01 Å.

Data collection: *SMART* (Bruker, 1997) for (I); *APEX2* (Bruker, 2004) for (II) and (III). For all compounds, cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*. Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994) for (I); *SHELXTL* (Sheldrick, 2008) for (II) and (III). For all compounds, program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3160). Services for accessing these data are described at the back of the journal.

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